# FACTORS INFLUENCING THE PREPARATION OF $TiO_2$ NANOPOWDERS FROM TITANIA SOL

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Submitted July 4, 2010; accepted October 30, 2010

**Keywords:** Plakett-Burman Design, Titania, methylene blue, Photocatalyst

*Titania nanoparticles with high photocatalytic activity were prepared from titanium alkoxide dissolved in alcohol and water under acidic conditions. The effects of the key parameters including (alkoxide/water) ratio, (alkoxide/alcohol) ratio, precursor type, solvent type, type and concentration of stabilizer, calcination temperature, presence of methylcellulose (MC) and hydrothermal treatment were studied. The optimal conditions were obtained through an experimental design technique. This technique is also used to find the main factors influencing the degradation of methylene blue (MB) and mass percent of anatase phase. The powders characteristics were investigated by XRD and Brunauer-Emmett-Teller (BET) methods. The X-ray diffraction studies showed that the product has anatase crystal structure with average particle size below 13 nm. The photocatalytic activities of the $TiO_2$ nanoparticles were assessed by the degradation of MB in aqueous solution. According to the obtained results, the kinetics of photocatalytic reaction followed pseudo-first-order model. The results showed that the main factors influencing the degradation of MB were the type of stabilizer, presence of MC, hydrothermal treatment, solvent type and calcination temperature. Specific surface areas of the nanoparticles were between 76-198 $m^2/g$.*

## INTRODUCTION

Waste water streams results from textile industry contain recalcitrant pollutant especially dyes. Removing colour from waste is often more important than other colourless organic substances, because the presence of small amount of dyes is clearly visible, and considerably influences the water environment [1]. Heterogeneous photocatalysis has been considered as a cost-effective alternative for the degradation of pollutant water. These alternative methods were based on the generation of highly reactive species such as hydroxyl radicals ($OH^{\bullet}$) that oxidize a wide range of organic pollutants [2].

Among various semiconducting materials (oxides, sulfides, etc.) most attention has been given to $TiO_2$ because of its novel ability to decompose organic contaminants in the atmosphere and water, as well as its chemical stability, with suitable band gap energy and biocompatibility [3-6]. The photocatalytic activity of $TiO_2$ depends on phase structure, crystallite size, specific surface area and pore structure [7]. The high crystallinity helps to prolong the recombination rate of the photoexcited electron and positive hole; hence strong reducing and oxidizing power of the photocatalyst. The high surface area would enhance adsorption of the target molecules on to the surface of the catalyst, the higher numbers of molecules are adsorbed the faster the rate of reaction [8]. $TiO_2$ has three main crystal phases: anatase, rutile and brookite. It is generally accepted that photocatalytic activity of anatase phase is higher than the other two phases (rutile and brookite) [9]. Typically, Titania obtained through sol-gel hydrolysis is amorphous and can be crystallized by heat treatment.

The photocatalytic activity in the aqueous system is usually evaluated by measuring the degradation rate of an organic molecule in the solution. Usually MB has been used as such a dye. The reasons for the choice of this particular dye are: (i) it is relatively stable against UV irradiation with out any photocatalyst, (ii) its stable under environmental conditions [10]. The classical approach of changing one medium component at a time is still being used but becomes impractical because it is time-consuming and has the risk of neglecting interactions among variables. The need for efficient methods for improvement of properties of titanium nanoparticles has led to adoption of the statistical experimental design; a good experimental design to be used for optimization employs the fewest number of measurements to get

the greatest amount of information. A Plackett-Burman statistical design is a reliable and efficient method for identifying critical variables because this method provides an efficient way of screening a large number of variables and it also identifies important parameter [11, 12].

In this work, $TiO_2$ nanoparticles were prepared through sol-gel procedure meanwhile the parameters were investigated according to Plackett-Burman statistical plan. In order to find appropriate conditions for preparation of titania nanoparticles, important parameters were investigated while photocatalytic activity and percent of anatase phase have been considered as responses. Furthermore, properties of samples such as particle size and surface area were investigated.

## EXPERIMENTAL

Plackett–Burman with 12 trials as shown in Table 1; a statistical experimental program is used for relevant statistical analyses. The operational parameters for our experiments are described in Table 2 (Column 1& 2). In order to calculate effects of each parameter on chosen responses, following equation can be used [13, 14]:

$$Effect_{(X)} = \frac{\frac{\Sigma R \text{ at high} X}{\text{No. of experiments}}}{2} - \frac{\frac{\Sigma R \text{ at low} X}{\text{No. of experiments}}}{2} \quad (1)$$

where $R$ is the response which refers to the percent of degradation of MB after 60 min and the percent of anatase phase. In addition X defines key parameters, mentioned earlier in Table 2.

### Materials and formulation

Titanium tetra iso propoxide (TTIP) (98%, Merck) and Titanium Butoxide (97%, Merck) were used as precursors. Iso-Propanol (99.5%, Merck) and Buthanol (99%, Merck) were used as solvents to prevent fast hydrolysis of titanium alkoxide. Methylcellulose (MC) was used as a dispersant and $HNO_3$ (65%, Merck) and $CH_3COOH$ (95%, Merck) were used as stabilizers.

Twelve samples were prepared according to Table 1 and 2. The procedure was as follows: titanium alkoxide was slowly added to alcohol and then; the mixture of titanium alkoxide & alcohol was placed in the oil-bath. The solution was then added to the acidic solution and refluxed under vigorous stirring (800 rpm) at 90 °C for 8 h. In the case of using MC, in separate container, methylcellulose solution (2 wt.% in distilled water) was prepared and then these two solutions (Titania sol and MC solution) were mixed and stirred for 1 hour at 90 °C. According to Table 1 and 2, after the hydrothermal treatment (Sample 2, 6, 7, 8, 10 and 11), the obtained suspensions were transferred in to dishes and dried at room temperature. The rest of them (Sample 1, 3, 4, 5, 9 and 12) were dried without hydrothermal treatment. All dried samples were calcined at designed temperature with a ramp rate of 2 °C $min^{-1}$ for 1 hour.

Table 1. Possible combinations of relevant factors of a Plackett-Burman design, (+) factor at high level, (–) factor at a low level (D and H are dummy factors).

| Sample No. | Parameter | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | D | E | F | G | H | I | J | K |
| 1 | + | + | – | + | + | + | – | – | – | + | – |
| 2 | – | + | + | – | + | + | + | – | – | – | + |
| 3 | + | – | + | + | – | + | + | + | – | – | – |
| 4 | – | + | – | + | + | – | + | + | + | – | – |
| 5 | – | – | + | – | + | + | – | + | + | + | – |
| 6 | – | – | – | + | – | + | + | – | + | + | + |
| 7 | + | – | – | – | + | – | + | + | – | + | + |
| 8 | + | + | – | – | – | + | – | + | + | – | + |
| 9 | + | + | + | – | – | – | + | – | + | + | – |
| 10 | – | + | + | + | – | – | – | + | – | + | + |
| 11 | + | – | + | + | + | – | – | – | + | – | + |
| 12 | – | – | – | – | – | – | – | – | – | – | – |

Table 2. Operational parameters and their levels for the preparation of Titania nanoparticles through experimental design and resulting effects.

| Parameter (label) | Low value (–) | High value (+) | Effect (Degradation of MB after 60 min) |
|---|---|---|---|
| Precursor (A) | Ti(But) | TTIP | 3.7 |
| Solvent (B) | Buthanol | Iso-Propanol | 6.1 |
| MC (C) | Off | On | 6.8 |
| $Ti/H_2O$(mol ratio) (E) | 0.008 | 0.005 | -2.9 |
| Ti/Solvent(mol ratio) (F) | 1.57 | 0.78 | -1.1 |
| Type of Stabilizer (G) | $HNO_3$ | $CH_3COOH$ | 8.9 |
| Calcination temperature (°C) (I) | 350 | 450 | 4.7 |
| Concentration of stabilizer (M) (J) | 0.068 | 0.103 | -3.3 |
| Hydrothermal treatment (K) | Off | On | 6.2 |

## Catalyst characterization

### *X-ray diffraction*

The XRD patterns were obtained via the Philips PW 1840 powder diffractometer using *cu kα* radiation and equipped with a Ni filter. Diffraction patterns of anatase, rutile and brookite phase were compared with reference to JCPDS powder diffraction files (21-1272, 21-1276, 29-1360). From the line broadening of the corresponding X-ray diffraction peaks and using the Scherrer's formula, the crystallite size has been estimated by:

$$D = \frac{K\lambda}{\beta Cos\theta} \tag{2}$$

where $D$ is the average crystallite size in nm, $\lambda$ is the wave length of the X-ray radiation (0.15406 nm for copper lamp), $K$ is constant usually taken as 0.89, $\beta$ is the line width at half maximum height in radians, and $\theta$ is the diffracting angle [15, 16].

The phase content of titania nanopowders can be calculated according to the following equations [7]:

$$W_A = \frac{K_A A_A}{K_A A_A + A_R + K_B A_B} \tag{3a}$$

$$W_R = \frac{A_R}{K_A A_A + A_R + K_B A_B} \tag{3b}$$

$$W_B = \frac{K_B A_B}{K_A A_A + A_R + K_B A_B} \tag{3c}$$

In these equations mass fractions of anatase, brookite and rutile are identified as $W_A$, $W_B$ and $W_R$. Also $K_A$ and $K_B$ are two constant values of 0.886 and 2.721, respectively. In addition, the intensity of the anatase (101), brookite (121) and rutile (110) strongest peaks are indicated by $A_A$, $A_B$ and $A_R$, respectively [7].

## Specific surface area

Specific surface area of the nanoparticles was measured by the dynamic Brunauer-Emmett-Teller (BET) method, in which the Nitrogen was adsorbed at -196°C using a Quantasorb surface area analyzer (Quantachrome Co.). All the samples were degassed at 300 °C for 2 hours prior to surface area measurement. The specific surface area values were calculated by the BET equation in the interval $0.05 \leq (P/P_o) \leq 0.35$ [17].

## Photocatalytic degradation of MB

The photocatalytic activity of the samples was estimated by decomposition of 20 ppm methylene blue by using 50 ppm of photocatalyst. The photoreactor consisted of a cylindrical glass reactor that a light source from 400 w high-pressure mercury lamp located in front of vessel. A magnetic stirrer was used to produce homogeneous reaction mixture before and during illumination. Degradation was monitored by taking aliquots at different time intervals. The UV-Vis absorption spectra of the samples were recorded with a UV-Vis spectrophotometer (UV/Vis-Beckman Du series-500) after and before illumination at different times at $\lambda_{max}$ = 665 nm. The degradation of methylene blue was calculated by using the following formula:

$$\% \text{ Degradation} = [(C_o\text{-}C)/C_o] \times 100 \tag{4}$$

where $C_o$ and C are initial concentration and the reaction concentration of MB, respectively. Photocatalytic reactions are considered as pseudo-first-order reaction [18, 19]. So, for kinetic study we can use the following expression:

$$\text{Ln}\,(C_o/C) = Kt \tag{5}$$

where K is the apparent reaction rate constant and $C_o$ and $C$ are initial concentration and the reaction concentration of MB, respectively [20-22].

## RESULTS AND DISCUSSION

The degradation results of MB after 60 min for all twelve samples are presented in Figure 1. The effects of each parameter (calculated by using equation 1) are shown in Table 2 (last column).

Different statistical methods are used to evaluate whether a given effect (parameter) is significant or not. The experimental student's test presented by this equation [$t_{value}$ = $effect/(SE)_e$] was applied to calculate the standard error $(SE)_e$ given by the following equation (using the dummy variables) [11,13,14];

$$(SE_e) = \left( \frac{\Sigma\,(effect_{dummy})^2}{No.\ of\ dummy\ variables} \right)^{1/2} \tag{6}$$

In accordance with Table 1, the two dummies (D and H parameters) were used as degree of freedom for calculating $(SE)_e$. Since all the parameters were coded as a (+) and (–), the absolute magnitude of the resulting coefficients ($t_{obs}$) can be used to rate the relative importance of the parameters. A parameter was

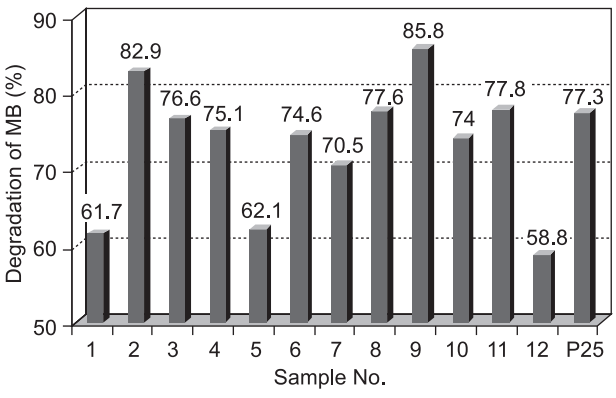


Figure 1. Degradation of MB after 60 min for prepared samples and P25.

considered significant if the value of the t-test were above a tabulated student's t-value ($t_{tab}$). The number of degrees of freedom and the applied significance level "α" will determine the $t_{value}$. A tabulated student's t-value around ±6.3 was selected for comparison which is a guide to predict the significance of each parameter [13, 14]. Standardized Pareto plot (Figure 2) represents the absolute value of $t_{value}$ of degradation of MB.

For each parameter, these results give rapid visual information on the magnitude of $t_{obs}$ (Figure 2). In fact, the magnitude of bar more than the $t_{tab}$ value reveals significant parameters. According to $t_{value} > t_{tab}$ and Figure 2, the most significant parameter was considered to be the type of stabilizer. In addition, the presence of MC, hydrothermal treatment, solvent type and calcination temperature were relatively significant parameters on degradation of synthesized samples, but the other parameters showed insignificant effects on these responses in the tested ranges.

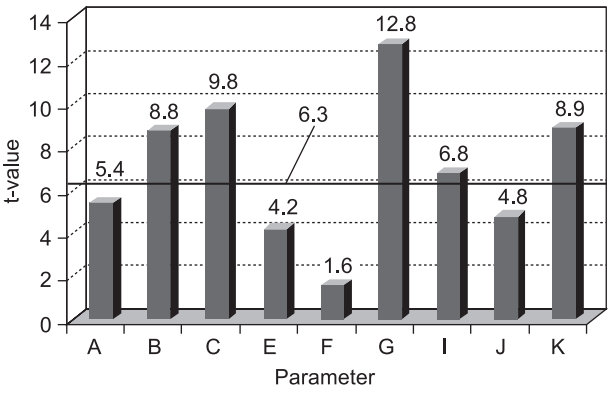


Figure 2. Standardized Pareto chart of effects on degradation of MB - estimation (SE) 0.69, $t_{tab}$ (0.05, 1) = 6.3, 90%.

Figure 3 shows the comparison of the apparent rate constant ($min^{-1}$) of sample 9 and P25 Degussa. It could be seen that sample 9, showed high photocatalytic activity with a rate constant of $2.3810^{-2}$ $min^{-1}$. Its photocatalytic activity is higher than that of P25 ($1.4410^{-2}$), which is well known to give a high photocatalytic activity [23]. This maybe attributed to the fact that the former had a large specific surface areas and smaller crystallite size as well as high crystallinity. The specific surface area and crystallite size of P25 were determined to be about 50 ($m^2g^{-1}$) and 30 (nm), respectively.

Figure 4 shows the XRD patterns of $TiO_2$ nanoparticles for all prepared samples. According to the full-width at half-maximum of XRD peaks, when the width was broader the crystallites exhibited smaller sizes. In other words, sharper XRD peak indicates a larger particle size or more well-ordered crystallites [24]. According to Table 3, crystallite size increased and specific surface area decreased considerably while calcination temperature enhanced.

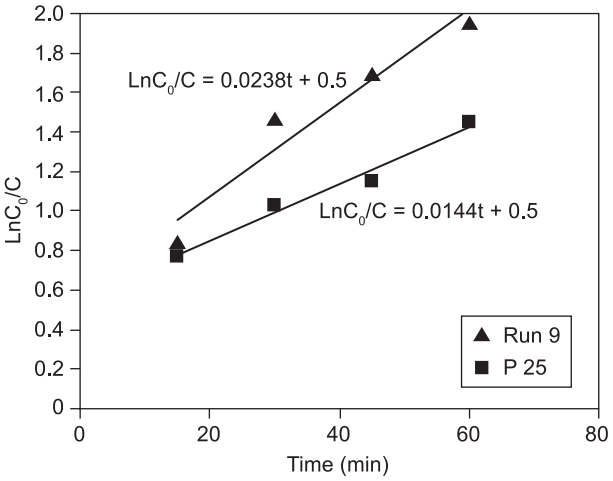


Figure 3. Dependence of the apparent rate constant (k, $min^{-1}$) for sample 9 and P25.

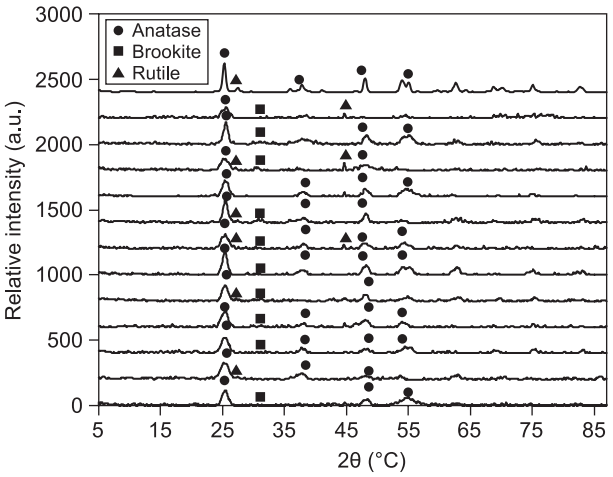


Figure 4. XRD patterns of $TiO_2$ nanoparticles and P25.

Table 3. Comparison of $TiO_2$ nanoparticles under various conditions according to experimental design.

| Sample No. | Surface area ($m^2g^{-1}$) | Crystallite size[a] (nm) | Crystallinity[b] (%) |
|---|---|---|---|
| 1 | 115 | 9.3 | 80.8 |
| 2 | 173 | 5.8 | 80.5 |
| 3 | 168 | 6.2 | 89.3 |
| 4 | 126 | 7.2 | 77.1 |
| 5 | 87 | 8.3 | 74.2 |
| 6 | 97 | 12 | 93.3 |
| 7 | 198 | 6 | 77.9 |
| 8 | 76 | 12.9 | 58.4 |
| 9 | 135 | 8.2 | 94.9 |
| 10 | 174 | 5.6 | 50 |
| 11 | 94 | 11.2 | 73.1 |
| 12 | 140 | 6.9 | 82.7 |

[a] *Calculated from XRD data using Eq.(2) for anatase phase.*
[b] *Calculated from XRD data using Eq.(3a).*

Several methods are available for identifying significant and effective parameter. Among these, Montgomery recommends using normal probability plots [25]. According to Figure 4 and by using equation 3, one can calculate the percent of phases for all samples. The normal probability plots of the effects were estimated and presented in Figure 5.

Figure 5 indicated that among the effective parameters, the main effects for the formation of anatase phase are type of stabilizer (G), hydrothermal treatment (K), Ti/solvent ratio (F), precursor (A) and presence of MB (C), because they deviate considerably from the line passing through the other points.

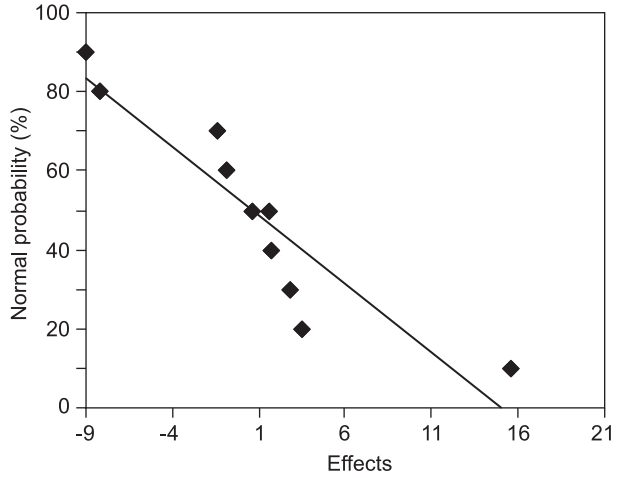


Figure 5. Normal probability plots for percent of anatase phase.

## CONCLUSIONS

The main factors influencing the nano sized Titania with high photocatalytic activity, prepared by a sol-gel process were investigated through an experimental design technique. The Plackett-Burman design was demonstrated to be a powerful tool for identify significant process factors with relatively few experiments. The statistical analysis showed that the significance of parameters for the degradation of MB follows the following order: type of stabilizer > presence of MC > hydrothermal treatment > type of solvent > calcination temperature and the other parameters are insignificant. Moreover the main factors influencing the percent of anatase phase are found to be the type of stabilizer (G), hydrothermal treatment (K), Ti/solvent ratio (F), precursor (A) and presence of MC (C) and the other parameters are not so effective. According to kinetic studies, prepared samples obey Pseudo-first-order reactions and rate constant of these reactions are dramatically more than P25.

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